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Core-shell structured 1,4-benzoquinone@TiO₂ cathode for lithium batteries

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ABSTRACT

Organic carbonyl compounds are considered as promising candidates for lithium batteries due to their high capacity and environmental friendliness. However, they suffer from serious dissolution in the electrolyte, leading to fast capacity decay. Here we report core-shell structured 1,4-benzoquinone@titanium dioxide (BQ@TiO₂) composite as cathode for lithium batteries. The composite cathode can deliver a high discharge capacity of 441.2 mA h/g at 50 mA/g and a high capacity retention of 80.7% after 100 cycles. The good cycling performance of BQ@TiO₂ composite can be attributed to the suppressed dissolution of BQ, which results from the physical confinement effect of TiO₂ shell and the strong interactions between BQ and TiO₂. Moreover, the combination of ex situ infrared spectra and density functional theory calculations reveals that the active redox sites of BQ are carbonyl groups. This work provides an alternative way to mitigate the dissolution of small carbonyl compounds and thus enhance their cycling stability.

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1. Introduction

Organic electrode materials especially carbonyl compounds have been widely investigated in lithium batteries owing to their high capacity, flexible structural design ability, and high abundance [1–6]. Among them, small quinones are one of the most competitive candidates because they possess considerable active sites and low molecular weight [7]. For example, the simplest quinone compound, 1,4-benzoquinone (BQ), can exhibit theoretical capacity as high as 496 mA h/g and average discharge voltage of 2.7 V, corresponding to high energy density of 1339 W h/kg (based on the mass of BQ) [8–10]. However, similar to other small carbonyl compounds, BQ is plagued by serious dissolution in organic electrolyte and inferior electronic conductivity, which lead to fast capacity deterioration and sluggish reaction kinetics [11–13].

Many strategies have been attempted to address the above problems [14], including polymerization [15,16], salt formation [17–19], grafting on the insoluble substrates [20,21], combining with carbon source [22,23], and adopting quasi/all-solid-state electrolyte [24,25]. Up to now, the reported approach to enhance the cycling stability of BQ is polymerization. Song et al. successfully synthesized poly(benzoquinonyl sulfide) (PBQS) by two steps [26]. The

PBQS cathode could exhibit long cycling life up to 1000 cycles, which is much better than pure BQ. However, the highest reversible capacity of PBQS is only 246 mA h/g because the carbonyl utilization is generally low in polymers and the introduction of inactive S atoms also inevitably decreases the capacity. Therefore, developing new methods to improve the cycling performance of BQ without sacrificing its capacity simultaneously are of great significance. Recently, polar shell host materials such as TiO₂ that exhibit strong interactions with the polysulfides in the Li–S battery systems have been studied and appear to be an effective approach to stabilizing the capacity [27–29]. To the best of our knowledge, there is no report about utilizing polar shell host materials to inhibit the dissolution of organic electrode materials. Thus, introducing the polar shell host structure to enhance the electrochemical performance of BQ would be very interesting.

We here report BQ@TiO₂ core-shell structured composite as cathode for lithium batteries. The special structure displays three main advantages as follows. (1) The TiO₂ shell can play a role in confining BQ materials physically. (2) The strong interactions between BQ and TiO₂ is helpful to mitigate the dissolution of BQ in the electrolyte. (3) The electronic conductivity of BQ could be enhanced because TiO₂ is a semi-conductor. As a result, the discharge capacity can retain 80.7% after 100 cycles at 50 mA/g. Additionally, the redox mechanism of the BQ@TiO₂ composites is revealed by ex situ infrared spectra (IR) and density functional theory (DFT) calculations.

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50 2. Experimental

51 2.1. Materials

52 Benzoquinone (Innochem Co.) was purified by sublimation-
 53 condensation method at 50 °C and the color of depurant BQ
 54 is bright yellow. Isopropanol, anhydrous ethanol, glycol dimethyl
 55 ether (DME), titanium (IV) isopropoxide (TIP) and ammonium
 56 hydroxide (28 wt%) were purchased from Macklin Corporation.
 57 Tetraethoxysilane (TEOS) and hexadecylamine (HDA) were pur-
 58 chased from Alfa Aesar Corporation. Aqueous hydrofluoric acid (HF,
 59 40 wt%) was purchased from Aladdin Corporation. Polytetrafluo-
 60 roethylene (PTFE, 60 wt%) aqueous emulsion was purchased from
 61 Shanghai Hesun Corporation.

62 2.2. Synthesis of SiO₂ nano-spheres template and hollow TiO₂ shell

63 In a typical fabrication process, seeding growth method was
 64 adopted to synthesize the even silica template [30]. In a round-

65 bottom flask, ultrapure water (23.5 mL), isopropanol (63.3 mL) and
 66 ammonia solution (13 mL, 28 wt%) were strongly stirred at a con-
 67 stant temperature of 35 °C by water bath. Then, TEOS (0.6 mL) was
 68 firstly dropwise added into the mixture solution. Once the TEOS
 69 solution was added, the mixture gradually became milky white
 70 color. After half an hour, additional TEOS (5 mL) was dropwise
 71 added once again. The isothermal process continued for 2 h.
 72 After preparation, water and ethanol were used to wash the silica
 73 spheres, respectively. Then, SiO₂ nano-spheres were obtained after
 74 dried under 60 °C in an oven.

75 Next, TiO₂ shell was synthesized by "hard-template" method.
 76 The as-prepared silica sphere acting as the template was coated
 77 by titanium dioxide and HDA. Silica nano-spheres (400 mg) were
 78 ultrasonically dispersed into ethanol (49 mL) in the round-bottom
 79 flask. HDA (400 mg) and ammonia solution (1 mL, 28 wt%) were
 80 mixed into the flask by mightily stirring. The mixture solution was
 81 stirred for half an hour at room temperature. Then TIP (1 mL) was
 82 added into the solution. After 2 h, the product was also washed
 83 using water and ethanol, respectively. The remnant solvent was

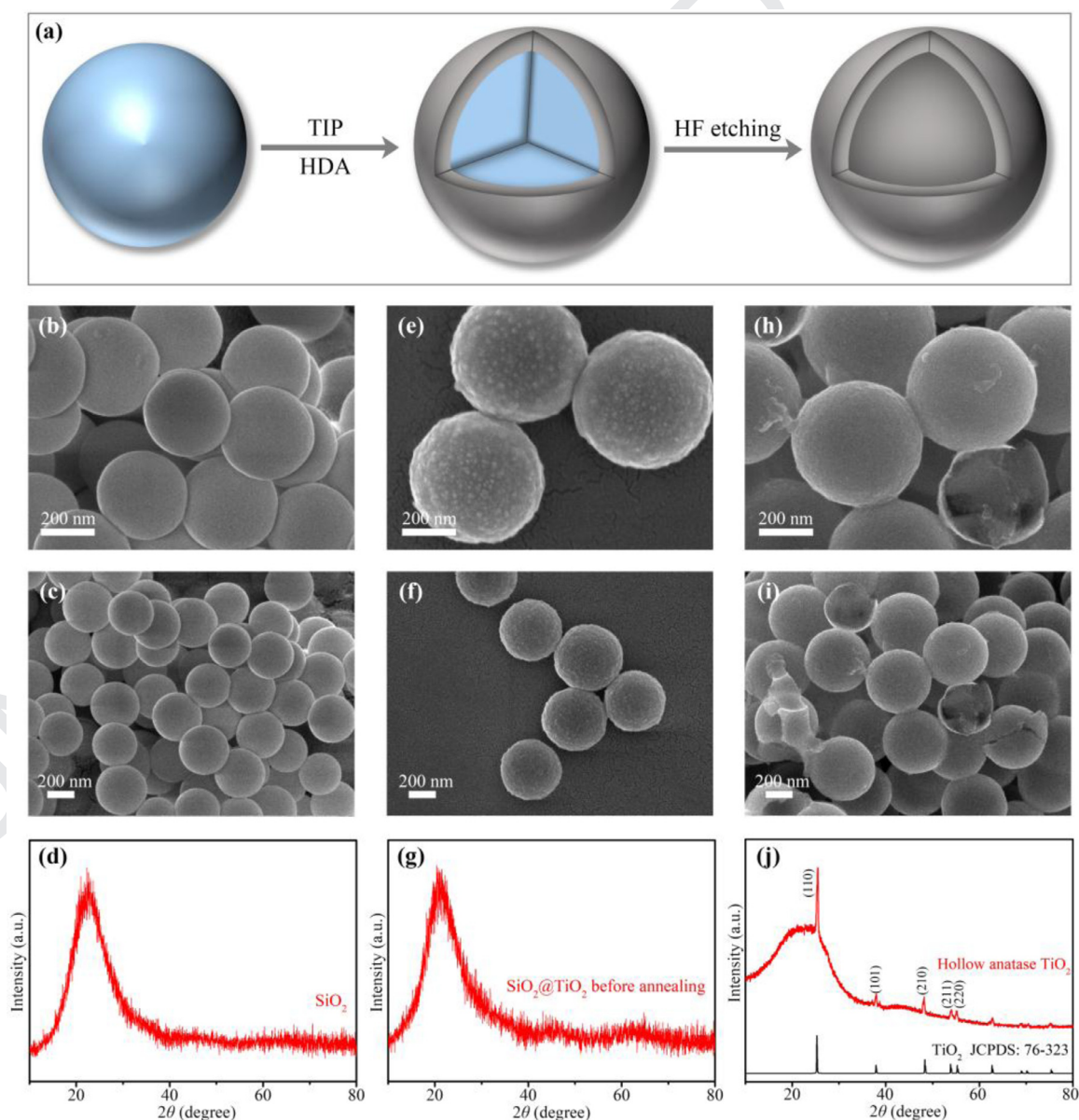


Fig. 1. (a) Schematic diagram of synthetic process of hollow TiO₂ nanoparticles; SEM images of SiO₂ nanospheres (b and c), SiO₂@TiO₂ nanoparticles (e and f), and hollow TiO₂ shells (h and i); XRD patterns of SiO₂ nanospheres (d), SiO₂@TiO₂ nanoparticles (g) and hollow TiO₂ shells (f), respectively.

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